Unit 4 : Macromolecules

No.

Date

① Macromolecules → large molecules formed by polymerization of small molecules (monomer).

Polymerization → chem. rxn - small molecules (monomer) combine to form larger molecule (polymer). with/without elimination of small molecules like H_2O, HCl, etc.

$$n\,(CH_2=CH_2) \xrightarrow{Polyn} -\!\!(CH_2-CH_2)\!\!-$$

$\alpha = \dfrac{\text{mol. wt of Polymeric network}}{\text{mol. wt of Repeating network}}$

Functionality → No. of bonding site / functional grp present in monomer.

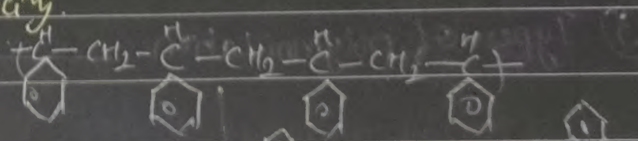
→ Bifunctional – 2

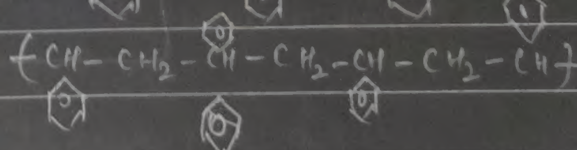
→ Trifunctional – 3

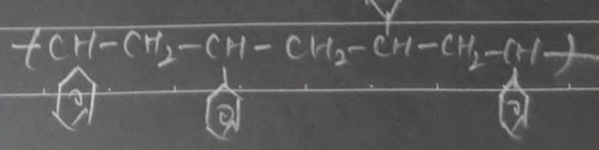
→ polyfunctional – >3

		f(x)
$CH_2=CH_2$	2 sites on both side	2
CH_3COOH	COOH	1
$H_2N-(CH_2)_6-NH_2$	NH_2	2
CH_2-OH / CH_2OH / CH_2OH	OH	3

Tacticity → orientation of monomeric / functional unit in a polymer can take place in orderly / disorderly manner w.r.t main chain is called tacticity.

→ Isotactic – same side 

→ Syndiotactic – alternating side 

→ Atactic – randomly 

Date

② Classification :

1) Based on Origin

Natural polymer
→ plants & animals
→ protein, starch, cellulose, etc

Semi synthetic
→ derived from natural polymer w. modification.
→ PVC, Nylon

Synthetic
→ man-made
→ plastic, synthetic rubber.

2) Based on Nomenclature :

Homopolymer
Same type of monomer
* Linear –M–M–M–
* Branched –M–M–M– (with –M branch)
* Cross-linked –M–M–M–
M–M–M–M–M
M–M–M–M–M–M

Heteropolymer.
more than 1 type
* Random –M_1–M_2–M_2–M_1–M_1–M_2
* Block –$M_1M_1M_2M_2M_1M_2M_2M_2$–
* graft –M_1–M_1–M_1–M_1– (with M_2–M_2–M_2 branch)
M_1 → main chain

Homochain poly
main chain madeup of same species
–C–C–C–C–

Heterochain poly.
main chain madeup of different species.
–C–O–C–O–

③ Types of polymerization → Addition [thermoplastic]
→ Condensation [thermosetting]

No.

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* **Addition :** → chem. rxn that yields exact copy of itself

(forms thermoplastic)

→ no elimination of molecule (small

$n(CH_2=CH_2) \xrightarrow{poly} -(CH_2-CH_2)-_n$ (Polyethyl

ethylene

$n(CH_2=\underset{Cl}{CH}) \xrightarrow{poly_n} -(CH_2-\underset{Cl}{CH})-_n$ (PV

vinyl chloride

Condensation : → chem. rxn that yields completely diff from the original compound.

(forms thermosetting)

→ elimination of molecule (small)

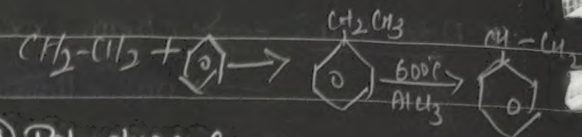
Example : Nylon 6,6 , PET, Polyurethane [Explained in next coming pages].

*

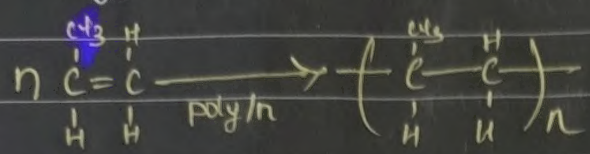
Thermo plastic	Thermo setting
⇒ Prep. by Addition	⇒ Prep. by Condensation
⇒ Linear polymer	⇒ Cross-linked Polymer.
⇒ Can be moulded into any shape (heating - soft, cooled - hard)	⇒ Can't be moulded easily. But they can be set to any shape quickly. (~~con~~ heating - hard; once hard cooling not possible
⇒ Weak intermolecular force of attraction & weak Covalent bond.	⇒ Strong intermolecular force of attraction and strong covalent Bond.
⇒ Soluble in Organic solvents.	⇒ Insoluble in Organic solvents
⇒ Eg : polyethylene, PVC.	⇒ Bakelite, polyster.

Addition Homochain	Condensation hetero chain
→ involves only 1 monomer	→ >2 monomers
→ gives exact copy of itself and no loss of simple molecule	→ form completely diff molecules.
→ same empirical formula	→ loss of simple molecule.
→ PVC, Teflon, polyethylene	→ diff. empirical formula
	→ Nylon 6,6, Bakelite.

Examples for Thermoplastic



① Polypropylene —



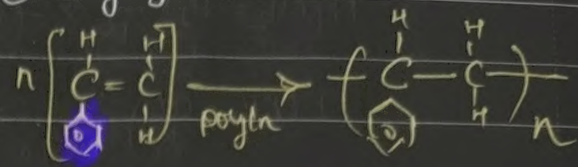
Prop: 1. Isotactic. Isohard hospital

2. Possess hardness, strength, stiffness.
3. Stiffer, harder, stronger than polyethylene.

Uses: * Rope, carpet (indoor/outdoor)

* hand bags, blankets
* furniture
* machine parts, water pipes.
* hospital sterilizable equipment.

② Poly styrene —

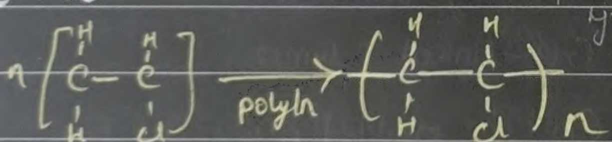


Prop: 1. Transparent translight resistant

2. Excellent chem, electrical, moisture resistance. Also acid.
3. light, stable, unique property of transmitting light through curved sections

Uses: Toys, button, radio/TV parts, refrigerator parts, lens, Indoor lighting panel

③ PVC — colour odour hard synthetic tyre.



Prop: 1. colourless, odourless.

2. Pure resin possess highly softening & greater stiffness and rigidity compared to polyethylene (but brittle)
3. Widely used in synthetic plastics.

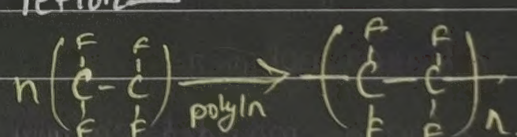
2 types < Rigid PVC / Plasticized PVC.

Uses:

Rigid: light fittings, safety helmets, tyres, cycle & bike mudguard, refrigerator components.

PPVC: Rain coats, curtains, cloth, toys, tool handles, radio ...

④ Teflon —



Prop: 1. Due to presence of highly electronegative fluorine atom results in strong attractive force b/w chain. That attractive force gives extreme toughness & high softening point.

2. high chem Resistance, high density.

Uses: * Insulating material for motor, transformer, cable wires.

* Gaskets, packed material, pump parts

Examples for Thermosetting

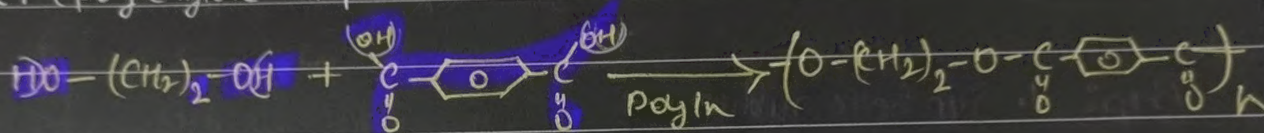
① Nylon 6,6.

$$H_2N-(CH_2)_6-NH_2 + \underset{\overset{\|}{O}}{\overset{(OH)}{C}}-CH_2-\underset{\overset{\|}{O}}{\overset{(OH)}{C}} \longrightarrow \left[HN-(CH_2)_6-\overset{H}{N}-\underset{\overset{\|}{O}}{C}-CH_2-\underset{\overset{\|}{O}}{C} \right]_n$$

Prop:
1. translucent property.
2. abarasion resistance.
3. high temp. solubility
4. insoluble in organic solvent

Uses
⇒ used in fibres.
⇒ use in making of carpets, dress, wires, etc

② PET (poly ethylene terepthalate)



Prop:
1. highly resistant to minerals and organic acids but less resistant to alkali
2. is a good fibre forming material and used as commercial fibre.

Uses
⇒ used as synthetic fibre.
⇒ making safety helmets.
⇒ " aircraft battry box.

③ Polyurethane.

$$OH-(CH_2)_2-OH + \overset{\overset{O}{\|}}{C}-N-(CH_2)_2-N-\overset{\overset{O}{\|}}{C} \longrightarrow \left[O-(CH_2)_2-O-\overset{\overset{O}{\|}}{C}-N-(CH_2)_2 \right.$$

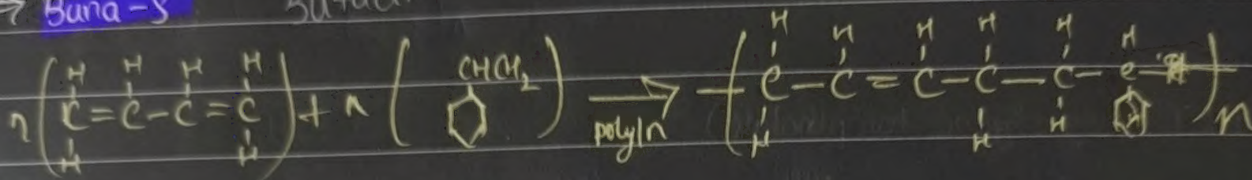
Prop:
1. high resistance for oxidation
2. " for organic solvents.
3. " heat, abrasion & chemicals

uses:
⇒ film walls, coating, foam
⇒ foundation garment, swimsuit.
⇒ used as leather substitutes

④ Synthetic Rubber:

* Man-made vulcanisable rubber like polymer.
* stretched force the length but return to same shape asap force is left.
* Eg: Buna-S

→ Buna-S   Butadiene styrene



Prop: 1. Synthetic rubber.

2. Abrasion resistant & Oxidization heavily.

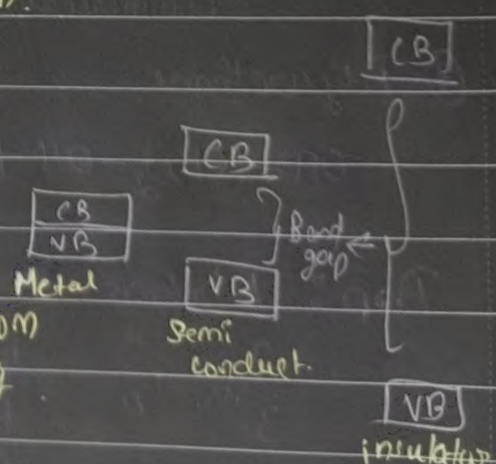
3. vulcanizable similar to natural rubber by sulphur.

(S ∝ vulcanizable)

Uses: * manufacture of tyres.

* gaskets, floor tiles & cable insulation.

Conducting polymer:

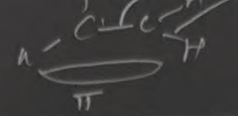


Valence Band — Outer orbit filled w. e^-

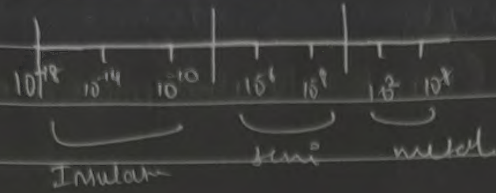
Conduction Band — region where free space for e^- from valence band to jump in during excess energy

Band gap — Energy diff b/w valence Band & Conduction Band.

(Band gap ∝ amt of energy for e^- transfer)



Fermi lvl – highest energy state occupied by e^- in material



Requirements for conducting polymer:
- ⇒ linear backbone
- ⇒ alternate double bond $-/=/-/=/-/=$
- ⇒ due to either π e^- or doped ingredients.

Characteristics:

- → Conduct electricity coz of π bond.
- → either metallic / semiconductor.
- → high electric conduction
- → In pure form low electric conductance (act like insulator)
- → Processability by dispersion.

Conducting Polymer

→ Intrinsically conducting — π bond, excess of e^-

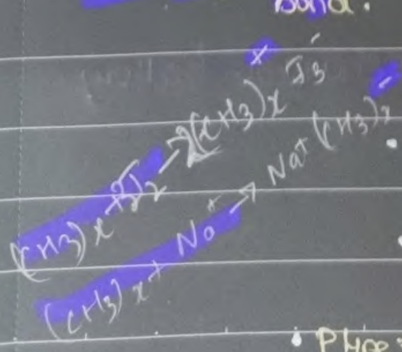
→ Extrinsically conducting → filled polymer / Bulk.

Intrinsically conducting:

- Conducting polymer having conjugate electric conduction due to π & double bond.
- Doped conducting polymer.
  - → adding substance inside polymer
  - → involve partial oxidation/reduction of π bond of polymer.
  - → substance either +ve/-ve.

Dopants are chem. substance used to ↑es electrical conductance by doping.

Doped conducting polymer → p type / n type.



p type:
- oxidizing agents
- create +ve charge on polymer
- P type = Polymer + Lewis acid (I, Cl)

n type:
- reducing agents
- Create -ve charge on polymer
- Polymer + Lewis Base = n type. (Na^+, K^+)

Factors affecting conductivity :

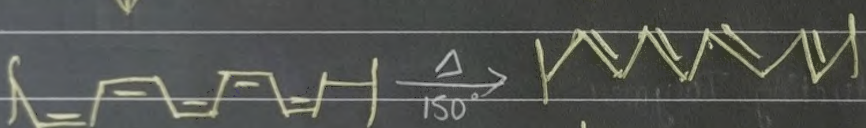
1) Conjugation length ∝ conductivity ↑
2) Doping level ↑ ∝ ↑ conductivity (until saturation point is reached)
3) Temp ↑ ∝ conductivity ↑

1) Poly acetylene $(C_2H_2)_n$

$CH \equiv CH$

Ziegler Natta (Catalyst)

-78°C | 150°C



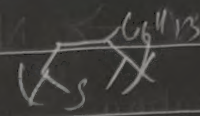
cis polymer
⇒ same sides
⇒ Copper coloured
⇒ Flexible & stretched.

trans-polyacetylene
⇒ alternating
⇒ silver coloured.
⇒ brittle

* Both highly thermal stable
* insoluble in organic solvent (Both)

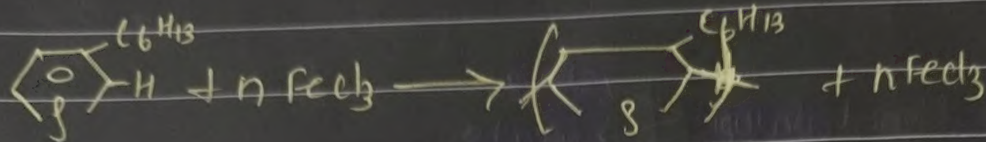
Uses: high conductivity - used in wiring & rechargeable battery
sensor to measure glucose conc.

2) P_3HT [poly(3- hexyl thiophene)] :



widely available, low cost, easy processability

Semi-crystalline polymer



⇒ 1:4 ratio, oxidation of 3hexylthiophine monomer.

① Rxn flask – Anhydrous $FeCl_3$ w chloroform & N and sealed

② using syringe 3hexyl thiophine added slowly.

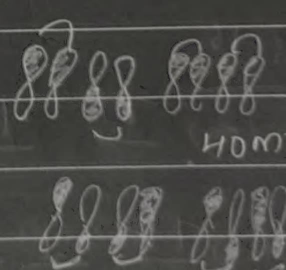
③ Carried out room temp; cooled w methanol.

HOMO → highest ~~energy molecular~~ occupied orbital

LUMO → ~~lowest~~ ~~unoccupied~~ next highest energy orbital that is empty

Prop: * wide availability

* low cost & easy processability
* P-type donor.
* In order to ↑ absorption of excess solar radiation
  1. Compare HOMO-LUMO
  2. ↓ LUMO
  3. ~~↑ HOMO~~



Uses: used as solar cell

" polymer batteries

" treatment in prion disease

" organic photovoltaic

LUMO energy > HOMO